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PLANETARY AERONOMY XV: TRANSPORT PROPERTIES AND SCATTERING IN MOLECULAR GASES

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ABSTRACT

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Experimental data on transport properties and scattering in molecular gases are usually interpreted assuming a spherically symmetric interaction potential and single channel (elastic) scattering. This procedure is analyzed and shown to be justifiable as a first approximation provided it is recognized that the generalization of transport theory to molecular gases involves the replacement of elastic cross sections by total cross sections and that the beam scattering data refer to total cross sections and not elastic cross sections. The distinction between total and elastic cross sections is especially significant for ion-molecule interactions at thermal velocities, since it implies a form for the long range interaction different from that which has been adopted. Some consequences of this difference in long range behaviour are described.

Explicit calculations are presented for the scattering of atomic hydrogen by molecular deuterium.

AUTHOR

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FIGURE CAPTIONS

Figure 1. Angular distribution for collisions between an H atom and D_2 molecule with incident energy 0.0625 eV;

curve A: elastic differential scattering cross section plotted against scattering angle;

curve B: inelastic differential scattering cross section plotted against scattering angle (the scale of inelastic cross section is $\frac{1}{20}$ scale of elastic cross section).

Figure 2. Elastic angular distributions for collisions between an H atom and D_2 molecule.

curve A: incident energy = 0.00625 eV;

curve B: incident energy = 0.03125 eV;

curve C: incident energy = 0.0625 eV.

Figure 3. Angular distributions for collisions between an H atom and D_2 molecule with incident energy 0.0625 eV.

Viscosity distribution $= 2\pi\ I\ (\theta)\ \sin\theta\ (1 - \cos^2\theta)$

curve A: elastic contribution;

curve a': inelastic contribution;

FIGURE CAPTIONS (continued)

Diffusion distribution = $2\pi\ I\ (\theta)\ \sin\theta\ (1 - \cos\theta)$

curve B: elastic contribution;

curve b': inelastic contribution.

1. Introduction

According to the Chapman-Enskog theory, the transport properties of dilute spherically symmetric gases depend upon the coefficients of diffusion, viscosity, thermal conductivity and thermal diffusivity. These transport coefficients may be expressed in terms of collision cross sections

$$Q_s = 2\pi \int_0^\pi I\ (\theta)\ (1 - \cos^s \theta)\ \sin\theta\ d\ \theta$$

where I (θ) is the differential cross section for the elastic scattering of one gas atom by another through an angle θ measured in the centre of mass system. The total elastic cross section is

$$Q = 2\pi \int_0^\pi I\ (\theta)\ \sin\theta\ d\ \theta .$$

Measurements of the scattering of beams of particles refer to the differential cross section I (θ) or to the total cross section for scattering through angles greater than some minimum angle θ_o:

$$Q\ (\theta) = 2\pi \int_{\theta_o}^\pi I\ (\theta)\ \sin\theta\ d\ \theta .$$

The differential cross section I (θ) can be evaluated from a knowledge of the interaction potential V (r) as a function of the separation r of the colliding particles. It is customary in the analysis of experimental data on transport coefficients and beam scattering to adopt an analytic representation of V (r) containing a number of disposable parameters and to choose the parameters so that the experimental data are reproduced. Having determined V (r) it may be used to predict other transport coefficients over wider temperature ranges and the procedure has proved very useful in extending experimental measurements.

It has also been followed in the analysis of molecular gases for which the interaction potential is not spherically symmetric and the scattering is not single channel (elastic) scattering. A detailed study is necessary in order to assess the significance of such analyses and of the effective interaction potentials that are derived.

2. Theory of Scattering

The scattering channels appropriate to a collision between two molecules can be labelled by the rotational angular momentum quantum numbers j_1 and j_2, characterizing the internal motions of the molecules, and the orbital angular momentum quantum number ℓ, characterizing the relative motion of the colliding pair. The interaction potential $V(\underset{\sim}{r})$ is a function of the position vector $\underset{\sim}{r}$ joining the two molecules, and it can usefully be written in the form

$$V(\underset{\sim}{r}) = v_o(r) + v_c(\underset{\sim}{r})$$

where $v_o(r)$ is obtained from $V(\underset{\sim}{r})$ by averaging over all orientations assuming that they are equally probable. The potential $v_c(\underset{\sim}{r})$ couples together different scattering channels $(\underline{j}_1, \underline{j}_2, \underline{\ell})$ and $(\underline{j}_1', \underline{j}_2', \underline{\ell}')$ such that

$$\underline{j}_1 + \underline{j}_2 + \underline{\ell} = \underline{j}_1' + \underline{j}_2' + \underline{\ell}' = \underline{J}$$

and gives rise to the possibility of inelastic rotational transitions.

The coupled equations which result from a partial wave expansion in angular wave functions corresponding to the total angular momentum quantum numbers J have been written down by Arthurs and Dalgarno[1] for atom-molecule collisions and by Gioumousis and Curtiss[2] for molecule-molecule collisions. We need not reproduce them here.

2.1 Weak Coupling

Arthurs and Dalgarno[1] have shown that if the coupling between channels is weak, the elastic cross sections Q and Q_s differ from those corresponding to scattering by the central field v_o (r) in second order in the coupling strengths, the first order changes vanishing essentially because v_c ($\underset{\sim}{r}$) vanishes when averaged over all orientations. The inelastic cross sections are clearly of second order in v_c ($\underset{\sim}{r}$). Thus, the assumptions of spherical symmetry and of single channel elastic scattering lead to second order errors only and the derived interaction potential can be identified as v_o (r), the average of the actual potential V ($\underset{\sim}{r}$) over all orientations.

However, the coupling is weak only for light molecules at low temperatures and a more typical situation involves a considerable range of impact parameters for which the coupling is strong.

2.2 Strong Coupling

The case of strong coupling has been discussed by Bernstein, Dalgarno, Massey and Percival.[3] They show that in the strong coupling region the total scattering cross section is insensitive to the details of the intermolecular potential and it has the same form as the elastic scattering cross section corresponding to a strong spherically symmetric potential. It follows that the analysis of experimental data on the basis of a spherically symmetric potential should not lead to gross error provided it is recognized that the cross sections occurring in the definitions of the transport coefficients and in the measurements of beam scattering are total cross sections, not elastic cross sections.

Some error may occur because the angular distributions of elastic and inelastic scattering are different. Whereas the inelastic angular distribution will not be very different from isotropic, the elastic angular distribution has a sharp forward peak associated with the shadow scattering (compare Figures 1, 2 and 3). Most beam scattering measurements refer to angles outside the shadow region so that the conventional analysis should be only slightly less accurate than for atomic gases when used for the prediction of the coefficients of diffusion and viscosity at high temperatures, which also do not involve any important contribution from the shadow region. Much greater error may result if the same potential is used to predict transport coefficients at lower temperatures at which the shadow region does contribute significantly to the collision cross sections. It should be stressed that the error does not arise from a mere lack of flexibility of the form of V (r) as for the atomic gas, but from the essential failure of the concept of an intermolecular (velocity-independent) potential.

Small errors may occur at lower temperatures in inferring one transport coefficient from measurements of another, since the associated collision cross sections weight differently the shadow and isotropic scattering regions. In particular, the use of viscosity data tends to

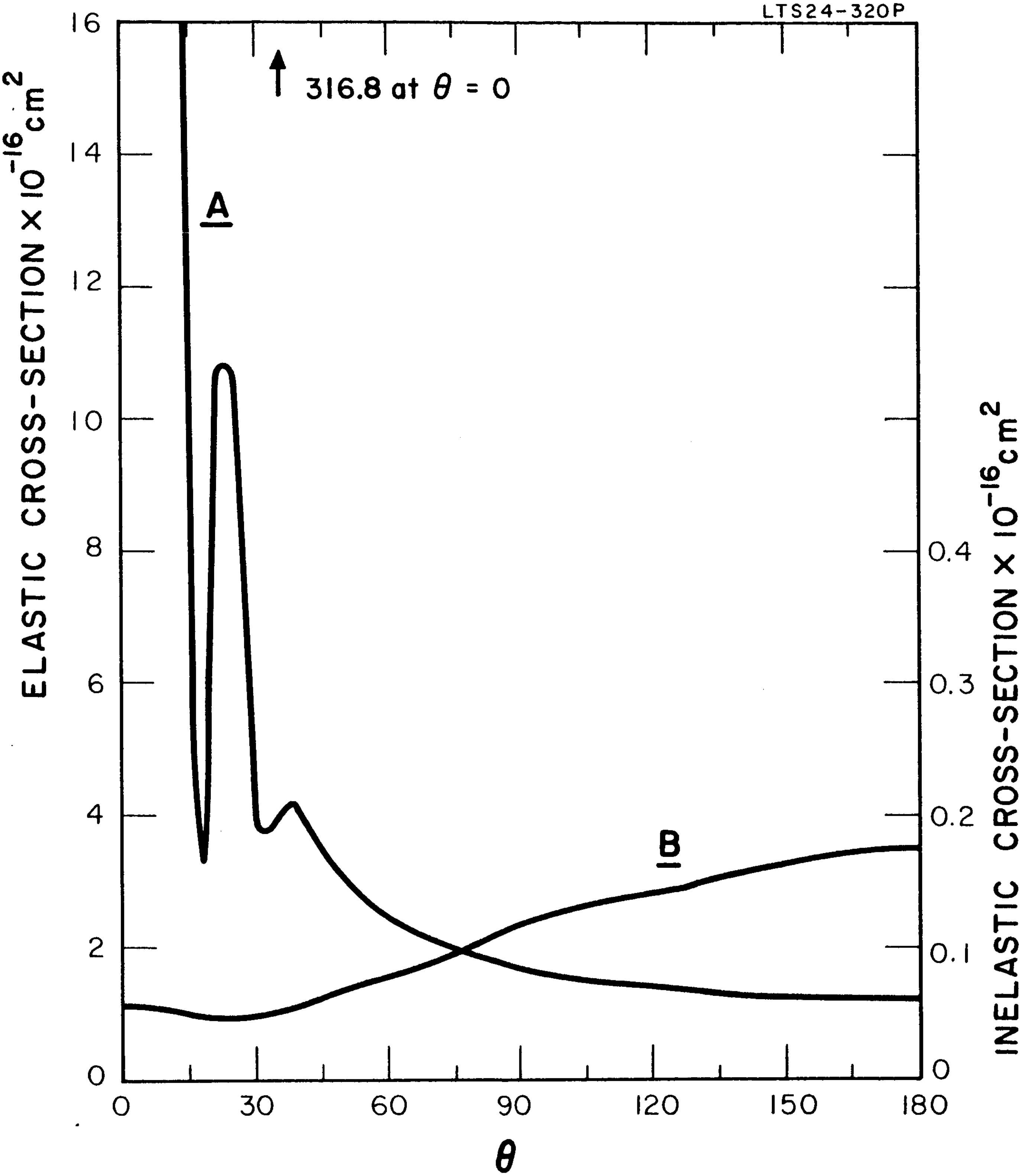
LTS24-320P
316.8 at θ = 0
A
B
ELASTIC CROSS-SECTION × 10^{-16} cm^2
INELASTIC CROSS-SECTION × 10^{-16} cm^2
θ
0
2
4
6
8
10
12
14
16
0
0.1
0.2
0.3
0.4
0
30
60
90
120
150
180

Figure 1

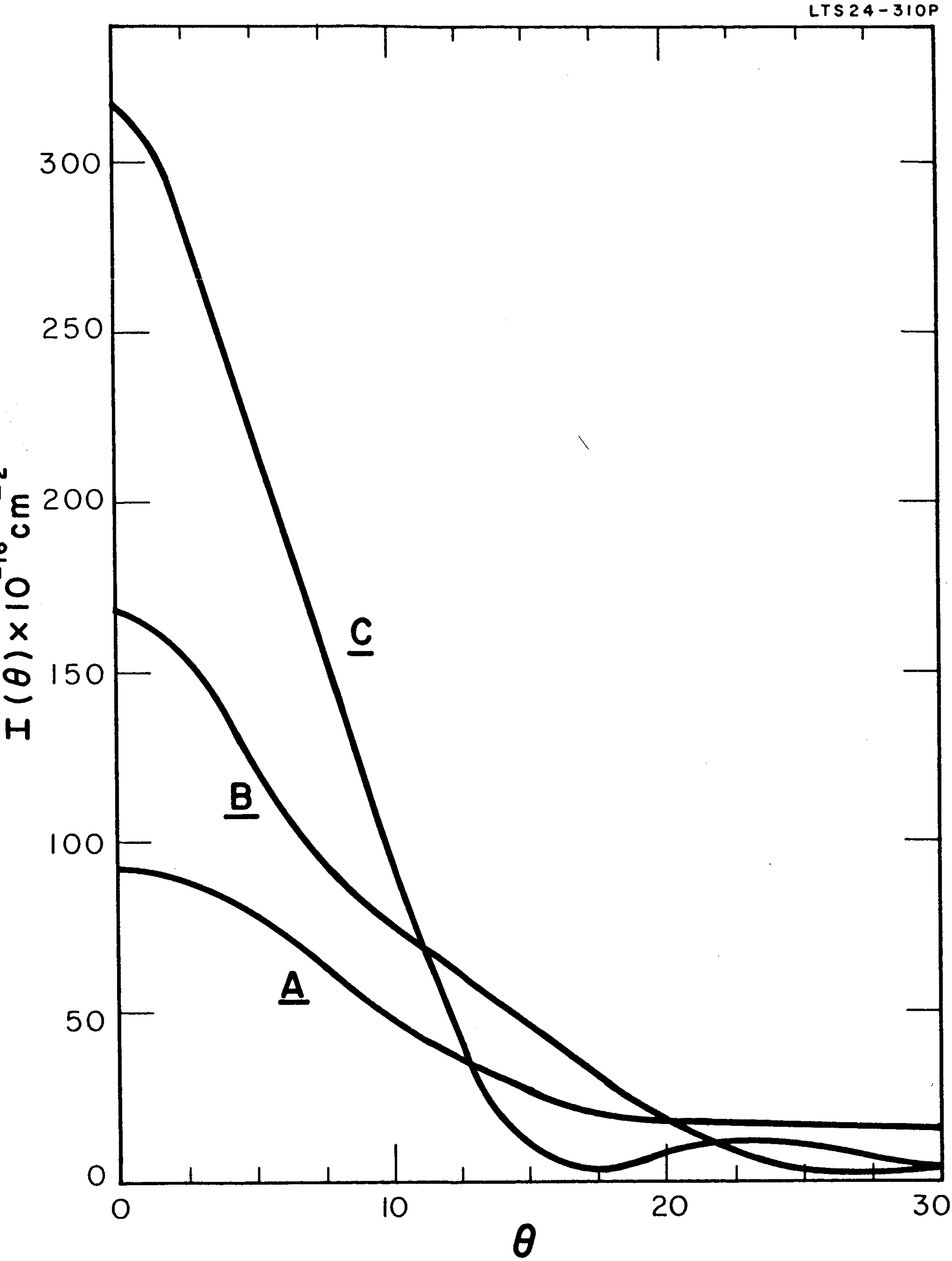

Figure 2

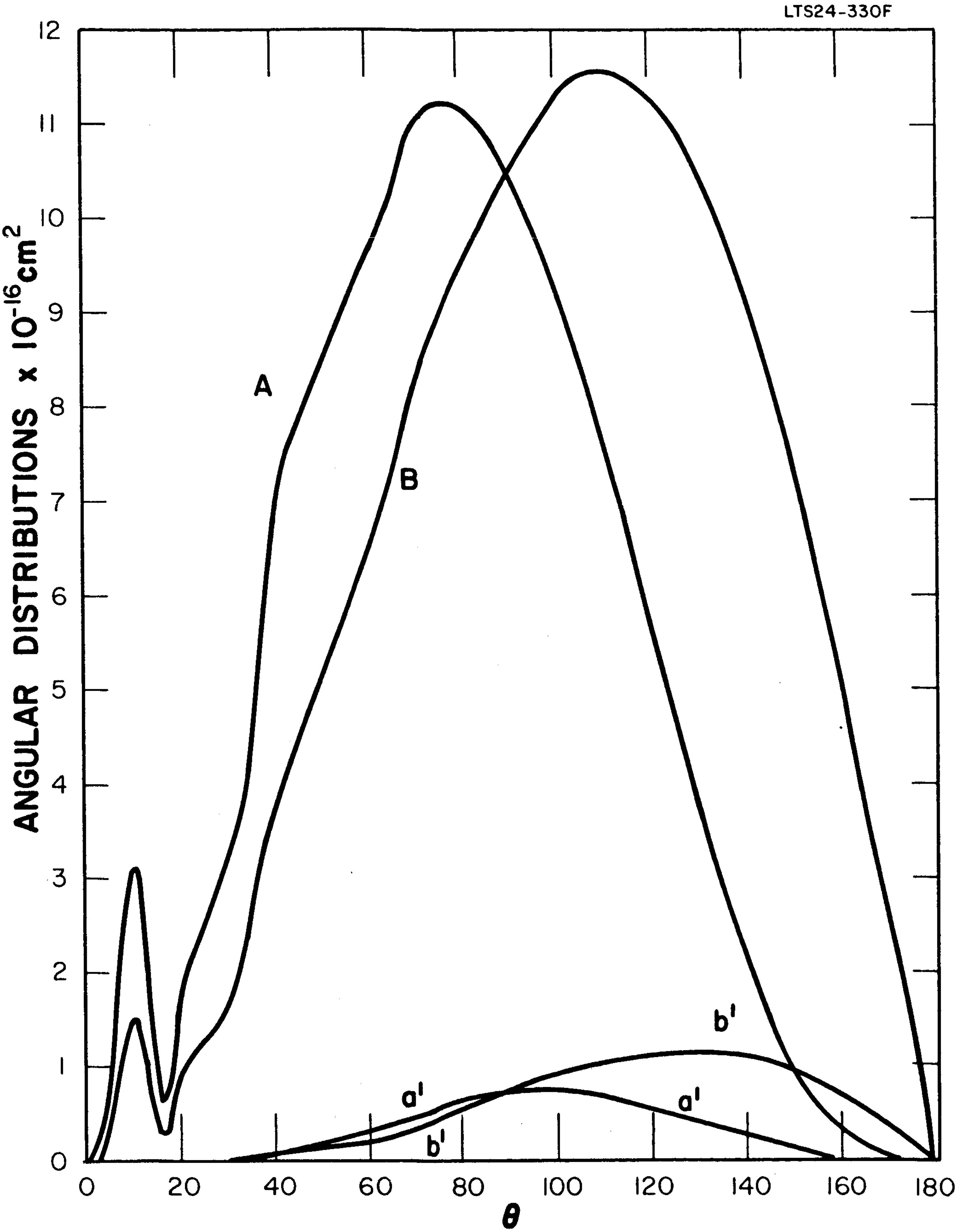
LTS24-330F
ANGULAR DISTRIBUTIONS x 10^-16 cm^2
A
B
a'
b'
θ
0
20
40
60
80
100
120
140
160
180
1
2
3
4
5
6
7
8
9
10
11
12

Figure 3

overestimate diffusion coefficients. This is opposite in sense to the observed discrepancies of Amdur, Ross and Mason,[4] Walker and Westenberg,[5] Westenberg and Frazier,[6] and Amdur and Shuler[7], the origin of which may be rather in the inappropriateness of the adopted analytic representations of V (r).

Thus, at large separations, the leading term of $V(\underset{\sim}{r})$ for a pair of neutral diatomic molecules decreases as r^{-3}, r^{-4} or r^{-5} depending upon whether both one or neither of the molecules has a permanent dipole moment. On averaging equally over all orientations, these terms vanish and the leading term is the spherically symmetric r^{-6} term that is usually adopted. If the scattering were mainly elastic in the important range of scattering angles, the choice could perhaps be justified (except at very low temperatures).* However, according to Bernstein <u>et al</u>.[3] up to half the total scattering may be inelastic and for the inelastic scattering there occurs no cancellation of the contributions from $v_c(\underset{\sim}{r})$.

There is a case of special interest which should be accessible to experimental verification. In the long range interaction of a positive or negative ion with a diatomic molecule, $v_o(r)$ decreases as r^{-4} and $v_c(\underset{\sim}{r})$ as r^{-2} or r^{-3}. If the effective interaction has the form of $v_o(r)$, then just as for an atomic gas, the mobility of an ion in a molecular gas tends to become independent of the gas temperature as the

*An interesting analysis of the effect of the orientation-dependent terms on the viscosity and second virial coefficient of hydrogen at very low temperatures has been presented by Niblett and Takayanagi.[10]

temperature decreases while if the effective interaction has the form of $v_c(\underset{\sim}{r})$, the mobility will tend to zero as the temperature decreases.

This marked difference between atomic and molecular gases was predicted by Arthurs and Dalgarno[8] from a consideration of elastic scattering only. The effect of $v_c(\underset{\sim}{r})$ on the elastic scattering is small until very low temperatures are reached. From the recognition that inelastic scattering is significant, it follows that the decrease of the mobility towards zero should set in at much higher temperatures than those implied by the formula given by Arthurs and Dalgarno.[8]

The predicted behaviour has been observed by Chanin, Phelps and Biondi,[9] for an ion, probably O_2^-, in O_2. The interpretation of this case is complicated by the possibility of charge transfer and measurements of the mobilities of various ions in unlike gases would provide a more certain test of the theoretical arguments.

3. Scattering in H_2 and D_2

The scattering of neutral particles in molecular hydrogen and in molecular deuterium at thermal velocities can be described by a weak-coupling approximation. Calculations of the inelastic angular distribution corresponding to the $j = 0$ to $j = 2$ rotational transitions have been carried out by Dalgarno, Henry and Roberts[11] using the formal scheme of Arthurs and Dalgarno.[1] Their results for the process

$$H + D_2\ (j=0) \rightarrow H + D_2\ (j=2)$$

at an impact energy of 0.0625 eV are reproduced in Figure 1.

We have computed the elastic angular distribution corresponding to scattering by D_2 in the $j = 0$ state and the results are shown in Figures 1 and 2. The elastic angular distribution is characterized by a sharp forward peak which decreases in angular extent as the impact velocity increases. The contributions of elastic and inelastic scattering at 0.0625 eV to the cross sections Q_1 and Q_2 effective in determining, respectively, the coefficients of diffusion and viscosity are shown in Figure 3. The contribution of the shadow scattering is suppressed and the contribution of the inelastic scattering is enhanced in comparison. Thus, whereas the total inelastic cross section is 2.5% of the total scattering cross section, the contribution of inelastic scattering to Q_1 is 7.5% of Q_1 and to Q_2 is 5.4% of Q_2.

An experiment in which a property of molecular hydrogen was carefully compared as a function of temperature with the same property of molecular deuterium would be of great interest. Because of the closer rotational spacing in D_2, the effect of inelastic scattering should become manifest at a lower temperature for D_2 than for H_2.

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